ON THE RELATIVE ABUNDANCE OF THE STABLE CARBON AND OXYGEN ISOTOPES IN THE RONA LIMESTONE, ROMANIA

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Introduction. The carbon and oxygen isotopic compositions of limestones provide criteria for the evaluation of the depositional environment. For Jurassic and younger samples (assumed to be non-recrystallized rocks) the best discrimination between marine and fresh water limestone is given by the equation[1]:

$$Z = 2.048(\delta^{13}C + 50) + 0.498\ (\delta^{18}O + 50) \quad (1)$$

where both $\delta^{13}C$ and $\delta^{18}O$ are relative to PDB. Limestone samples with a Z value above 120 would be classified as marine, while those with Z below 120 as fresh-water types.

Rona Limestone (Upper Paleocene-Lower Eocene) outcropping on a small area in the northwestern part of Transylvania is a local lacustrine facies within the Jibou Formation, which is divided into the Lower Variegated Member and the Upper Variegated Member. Recently a sequence containing a marine nano-plankton assemblage was identified in the basal layers of the Rona deposits.[2] From a mineralogical and genetic point of view, particularly noteworthy is the presence of siliceous nodules surrounded by a green clay coating. This is a unique paragenesis in the Romanian references. In the lower part of the succession at about 10 m from the bottom of the classical Rona profile these siliceous nodules ("septaria") of spherical to ellipsoidal morphologies are hosted by a 30-40 cm thick level of carbonate rock . The "septaria" are of gemological interest.[3] They are always surrounded by an intensely colored green clay layer (0.5-1 cm thick).

The goal of this study was to check, by isotopic geochemistry means, if a certain environmental signature is present to clarify if there is a marine influence in the samples under study, as suggested by Mészaros[2] and to define the environment of formation of the green clay and of the host-rock at the level of the siliceous "septaria".

Samples and analytical methods. Ten samples, including nine carbonate rocks and one (R28V) green clay surrounding the siliceous nodules, were collected from the classical outcrop near Rona village. Sample R28 represents the carbonate rock that hosts the siliceous "septaria". The samples were primarily analyzed from a mineralogical and petrographical point of view by the means of optical microscopy on thin sections and X-ray diffraction. Sedimentological observations were done in the field and by microscope.

In order to perform the carbon and oxygen isotopes measurements, samples were crushed to 100 μm mesh size and heated for about 30 minutes at 400º C to drive off volatile organic compounds. The CO_2 for mass spectrometer analysis was obtained by reacting the carbonate with 100% phosphoric acid at 25º C. The acidic attack was performed for 1h, to prevent a contribution of the C and O isotopes from the dolomite in the resulting CO_2. Thus, we suggest that the isotopic compositions are indicative only of the syngenetic processes which lead to the formation of calcite and probably are not influenced by the diagenetic environment that transformed part of the calcite into dolomite. The gas was collected, purified and analyzed in an ATLAS 86 mass spectrometer with a double collector. Measured data were corrected by means of the formula of Craig. The random analytical error is less than 0.1 ‰. Recorded δ values are the mean values of replicate runs.

Results and Discussion. According to the petrographic and sedimentological features, the carbonate facies are stacked like transgressive-regressive cycles, two main lithofacies associations being recognizable in a sequence[4]:

- Lacustrine association, with lime mudstone to packstone having scarce mollusks and charophyte debris, interbedded with black-greenish shales sometimes organic rich. The lack of bioturbations at some levels indicates water stratification and anoxia.
- Palustrine association, with pellet and intraclast grainstones or packstones, the intraclasts being reworked fragments of brecciated sediments exposed at lake margins. Pedogenetically-modified limestones are characterized by development of calcareous soils, exhibiting features such as brecciation, root tubules, microkarst, various cavities or iron oxide mottling.

The processes of dolomitization which were noticed in several carbonate sequences argue for an advanced degree of diagenesis.

The diffractograms on the nine carbonate-rich samples indicate the dominance (60-90 %) of calcite and dolomite in various ratios; clay minerals (5-30 %) and quartz (< 5 %) are also present. Thus, from a petrographic point of view the samples could be defined as limestones (R20, R25, R28, R35), dolomitic limestone (R6) and marls (R1, R16, R32, R46). Sample R28V represents a carbonitic clay (30 % carbonate minerals, very poorly crystallized) with a relatively high content of quartz (10 %).

Table 1.Carbon and oxygen isotope ratios and calculated Z parameter

Sample	$\delta^{13}C$ vs. PDB	$\delta^{18}O$ vs. PDB	Z
R1	-4.02	-14.13	113.66
R6	-5.11	-13.72	111.61
R16	-4.15	-14.78	113.08
R20	-5.40	-11.33	112.19
R25	-6.07	-13.39	109.76
R28	-4.91	-15.68	111.03
R28V	-6.78	-14.60	107.6
R32	-5.49	-8.62	113.3
R35	-4.56	-19.20	110.01
R46	-3.12	-9.41	117.89

The carbon and oxygen isotope data are reported as δ (‰) relative to the PDB standard in Table 1. All the $\delta^{13}C$ values are typical of fresh water carbonates, all being below -3 ‰. Along the profile, some trends can be noticed: 1) in the basal part there is a systematic variation of the $\delta^{13}C$ vs. PDB values; theoretically this means a relatively enrichment in ^{13}C in samples R1, R16, and enrichment in ^{12}C (of an organic origin) in samples R6, R20, R25. The differences are relatively small, but they are above the random analytical error. The geological meaning of this fact could be related to the rythmical changes between lacustrine and palustrine environments; 2) in the upper part of the analyzed profile a trend of decreasing of the $\delta^{13}C$ values is noticeable from samples R32 to R46. This is due to a gradual enrichment in ^{12}C, which could be explained by progressive restriction of palustrine environments; 3) when comparing samples R28 (carbonate host-rock) with R28V (green clay coating the "septaria"), there are quite different carbon isotopic ratios. In fact sample R28V registers the lowest $\delta^{13}C$ value (-6.78 ‰) in the samples under study, while sample R28 has a $\delta^{13}C$ value typical for the carbonate succession along the profile. This fact could be the result of various causes, such as the different mineralogical nature of the samples (R28V is a clay-dominated sample, fact which might have lead to different isotopic fractionation patterns), or the different environmental conditions of formation - a primary genesis is assumed for the host-rock while the green clay probably formed in the diagenetic stage.

The diffractometric similitude of the green clay with the clay fraction of the carbonate rocks supports the idea of a diagenetic remobilization and concentration of the clay content of the primary rock, having as a result the formation of the green coatings around the siliceous nodules.

In the case of the oxygen isotopes, the limits of variation of the $\delta^{18}O$ vs. PDB values range between (-8.62 – -19.20) ‰ and they are also indicative for fresh water carbonates. No trend was noticed along the profile. When comparing the values for samples R28V vs. R28, a slight enrichment in ^{18}O can be noticed in the green clay (sample R28V) as compared to the carbonate host-rock.

The samples from Rona are remarkable due to their relatively low $\delta^{18}O$ vs. PDB ratios (< -10 ‰). These values suggest a relatively anomalous content of ^{16}O in most of our samples (excepting R32, R46). A relationship between the mineralogical composition and the $\delta^{18}O$ values could not be identified. Thus, the cause of this fractionation pattern cannot be explained based on the present data.

The synthetic Z parameter based on both $\delta^{13}C$ and $\delta^{18}O$ ratios indicates, as expected, values characterizing the fresh water carbonates (between 107.6 – 117.89) in the case of all the analyzed samples.

In conclusion the oxygen and carbon data on samples from Rona limestone indicate a fresh-water depositional environment, with $Z<120$. The average carbon isotopic composition (-4.91‰) is significant for fresh-water carbonates of the Tertiary period, in general.The corresponding $\delta^{13}C$ and $\delta^{18}O$ values obtained for the carbonate minerals (30 % of the rock mass) in the green clay surrounding the siliceous "septaria" (R28V) indicate a fresh-water carbonate paleoenvironment.

Rferences

1. Keith M. L., Weber Y. N. (1964). Carbon and oxygen isotopic composition of selected limestone and fossils. *Geochem. Cosm. Acta,* **28**, 1787-1816.
2. Mészaros N. (1995). Marine deposits in the continental deposits of the Jibou Formation. *Studii şi Cercetări*, **1**, 59-61. Muzeul Județean Bistrița, Ed. Carpatica, Cluj-Napoca.
3. Ghiurcă V.(2000). Septaria silicieux de Roumanie. *Minéraux & Fossiles*, **289**, 25-30.

4. Pop Dana, Hosu A., Dărăban L., Constantinescu Ş. (1995). Mineralogical characterization of the green clay from the Rona limestone. *Rom. J. Mineralogy*, **77**, Suppl. 1, p. 36.